

[54] **SUBSTANTIVE POLYMERIC SUNSCREEN COMPOSITION**

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[56] **References Cited**

UNITED STATES PATENTS

2,887,116	5/1959	Wooding.....	424/78 X
3,238,138	3/1966	Braunwarth et al.	424/60
3,529,055	9/1970	Skouttchi et al.....	424/59 X
3,600,350	8/1971	Kwolek	260/78 A
3,622,545	11/1971	Foldi et al.....	260/78 A

3,642,572 2/1972 Endees et al. 260/78 A

FOREIGN PATENTS OR APPLICATIONS

774,110 5/1957 Great Britain 424/78

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[57]

ABSTRACT

Sunscreening compositions for topical application to the skin comprising a cosmetic carrier material containing a polymeric reaction product of a para-dialkylamino benzoyl halide and a polyethylenimine. These sunscreening compositions, when applied to the skin of the user, form a film of the polymeric reaction product which is highly effective in protecting human skin from erythema-inducing ultraviolet radiation and is resistant to removal from the skin by water or perspiration.

9 Claims, No Drawings

SUBSTANTIVE POLYMERIC SUNSCREEN COMPOSITION

BACKGROUND OF THE INVENTION

It is widely desirable in our society to secure tanning of the skin for purposes of appearance by sunbathing or other means. In order to enable or aid a person to subject themselves to tanning by such rays, several so-called sunscreens compositions have been made available to diminish or avoid the discomfort and dangers of erythema which may be simultaneously produced. It is well known that the ultraviolet radiation produced by the sun between the wavelengths of about 280 millimicrons to about 320 millimicrons are responsible for the distressing burning which is suffered by over-exposure. The ultraviolet radiation of longer wavelengths of up to about 420 millimicrons causes the aesthetically desirable tanning coloration of the skin.

It has been known by those skilled in the art that various compounds are useful to absorb the undesirable ultraviolet radiation ranging from 280 millimicrons to 320 millimicrons. Various aminobenzoic acid and substituted aminobenzoic acids are known to have the quality of absorbing the undesirable ultraviolet rays while transmitting those more desirable sun tanning producing rays. Also, the derivatives of para-aminobenzoic acid such as the dimethyl aminobenzoic acids have been used in the past in sun tanning compositions. It is also known that esters of P-aminobenzoic acid such as the methyl, ethyl or propyl p-amino benzoate as well as those esters formed from higher alkyl alcohols have valuable sun-screening effects. Each of these compounds while having desirable properties are not ideal for the purpose intended. They lack one or more of such desirable characteristics as solubility in cosmetic carriers at low temperatures, nonstaining of fabrics, stability on storage, stability on exposure to ultraviolet or visual radiation, resistance to oxidation to air. Moreover, compounds useful in absorbing erythema-causing rays are, when topically applied in the various known forms, easily removed from the skin by salt or fresh water.

In as much as sunscreens compositions are generally used in hot weather and at beach and water facilities where people enjoy bathing activities, such compositions which are removed by water have limited effectiveness. Even where artificially induced rays, such as by commercially available sun lamps, are used the heat causes the user to perspire which erodes the sunscreens agents away.

Sunscreens formulations have been produced in attempts to overcome the substantive instability of the foregoing described sunscreens materials. Ethylenically unsaturated ultraviolet absorbing compounds have been polymerized in attempts to make a substantive sunscreens material. These materials have the disadvantages in that they may contain small entrained quantities of harmful monomeric material or are polymerized under conditions which reduce the sunscreens ability of the resultant product.

SUMMARY OF THE INVENTION

It has now been found that sunscreens formulations which are useful in absorbing the erythema-producing rays of the sun are formed from a polymeric reaction product produced from para-dialkyl aminobenzoyl halides and polyethylenimines. The polymeric product

thus formed can be encompassed into any of the various cosmetic carrier materials known to be useful by the practitioner. Such polymeric products, when topically applied to the human skin, will form a film material which will resist removal from the skin by the action of salt or fresh water or perspiration.

Sunscreens formulations containing the polyethylenimine-para-dialkylaminobenzoyl halide reaction product are capable of screening harmful ultraviolet radiation while permitting transmission of the beneficial rays. In this manner the individual may subject himself to sunlight to cause the aesthetically desirable tanning of the skin while alleviating the problems of sunburn or erythema which is usually accompanied by discomfort and pain. The formulations containing the polymeric product described herein forms when, topically applied, a film material which adheres to the skin and resists removal therefrom even when subjected to the action of fresh or salt water or through perspiration of the individual. These compositions are, therefore, long lasting and need not be applied numerous times to insure proper protection.

DETAILED DESCRIPTION OF THE INVENTION

The material which has herein been found to be an excellent sunscreens agent is produced from the reaction of polyethylenimine and a para-dialkylaminobenzoyl halide. The para-dialkylaminobenzoyl halide may contain alkyl groups having from 1 to 4 carbon atoms such as methyl, ethyl, n-propyl or n-butyl groups and the like. The preferred compounds have alkyl groups each having one or two carbon atoms. These alkyl groups are attached to the nitrogen atom via a primary covalent bond and thus form a dialkylamino radical which is preferably attached to the benzene ring in the para position with respect to the halocarbonyl group. The halogen atom of the halocarbonyl group may be chlorine, bromine, fluorine or iodine. the chloro derivative is preferred due to its ease of handling, accessibility and reactivity.

Polyethylenimine is a commercially available material which is produced by the catalytic reaction of the cyclic compound, ethylenimine. Although the monomeric material, ethylenimine, is highly toxic, polyethylenimine has been found to be nontoxic to humans. This material is produced in a wide range of molecular weights ranging from about 500 to about 100,000 average molecular weight. The exact polyethylenimine used as the precursor for the substantive sunscreen material described herein may be any of the commercially available products. Lower molecular weight (about 500 to about 2,500) materials, available in anhydrous form, are particularly useful due to ease of handling when reacting with benzoyl halides.

The reaction product of polyethylenimine and a para-dialkylaminobenzoyl halide forms a polymeric material which may be described as poly(para-dialkylaminobenzoyl)ethylenimine. The polymeric product may be formed in any conventional manner in which halocarbonyls are reacted with primary and secondary amines. The hydrogen chloride byproduct which is formed may be neutralized by any known means such as by adding to the reaction mixture a compound such as sodium carbonate which will react in situ with the hydrogen chloride and will form products which can easily be separated from the desired polymeric material. Alternately, compounds may be added

to the reaction mixture after the desired product has been formed to neutralize any hydrogen chloride by-product entrained in the mixture. This may be done by utilizing ion exchange resins or by using alkalis such as sodium hydroxide.

The resulting polymeric material found useful herein include copolymers of polyethyleneimine containing copolymeric materials used as poly(p-dimethylaminobenzoyl)ethylenimine, poly(p-diethylaminobenzoyl)ethylenimine, poly[p-di(n-propyl)aminobenzoyl]ethylenimine, poly[p-di(isopropyl)aminobenzoyl]ethylenimine and the like as well as interpolymers having two or more substituted polyethylenimines in the same polymeric material such as poly[ethylenimine] [(p-dimethylaminobenzoyl)ethylenimine] [(p-diethylaminobenzoyl)ethylenimine] and the like.

The polymeric reaction products formed contain paradialkylaminobenzoyl radicals pendant to the polyethylenimine polymeric backbone. These pendant groups may be attached to the primary and/or the secondary amines of the polymer backbone. All of the polymeric reaction products have, when tested, highly selective absorption qualities for radiation in the ultraviolet wavelength range between about 280 millimicrons to about 320 millimicrons. This range of radiation is known to cause the onset of sunburn or erythema on human skin. Applicant's polymeric reaction products, when applied to the skin, in any convenient form protects the skin from these harmful radiations by forming a substantive film which absorbs the undesirable radiation.

The amount of para-dialkyl aminobenzoyl halide which is allowed to react with the polymeric backbone material may be of such quantity as to cause the polymeric product formed to have from about 5 to about 80 weight per cent dialkylaminobenzoyl radical pendant groups based on the total weight of the polymeric reaction product. Higher percentages of these pendant groups may be used although are not normally necessary to form an effective material. The exact percent of these pendant groups which may be incorporated onto the polymeric backbone is only limited by the amount of amino groups located thereon and the type of formulation onto which these products are to be used. It is realized that the radicals containing the higher alkyl groups will naturally be less in number for the same weight percentage. Therefore, higher weight percentages of these radicals will be needed to produce the same protection as radicals containing lower alkyl groups such as the dimethylaminobenzoyl radical.

Polyethylenimine may be reacted with one or more than one specie of dialkylaminobenzoyl halide either simultaneously or successively thereby forming a polymer reaction product having one specie of pendant group or having a mixture of dialkylaminobenzoyl groups.

Applicant's polymeric reaction product containing the selective ultraviolet absorption groups have been found to be highly effective suncreening agents in that they selectively absorb the harmful erythema producing rays while transmitting the more desirable tanning rays to the skin. These polymeric products readily form a film when applied to the skin which adheres thereto and is resistant to removal from the skin by the action of fresh water, perspiration, or salt water and, therefore, is more durable under conditions which are most

commonly found at the sea shore or the poolside. The polyethylenimine substrate which acts as a binder to the keratin surface of the skin and allows the paradialkylbenzoyl pendant groups to impart suncreening activity is longlasting and need not be applied periodically by the individual after each contact with the water nor periodically due to the action of body perspiration. The polymeric suncreening agent may have pendant groups which are all the same such as the dimethylaminobenzoyl radical or, alternatively, mixtures of dialkylaminobenzoyl halides may be reacted with polyethylenimine to form a mixed dialkylaminobenzoyl polyethylenimine polymeric material.

The polymeric material containing from about 5 to about 80 weight per cent pendant groups on the polymeric backbone may be combined with additional materials to form a suncreening composition. These compositions may contain from 1 percent to about 50 percent of the polymeric reaction product based on the weight of the total composition. Compositions containing from 1 percent to 25 percent of the polymer have been found satisfactory under normal conditions. The exact amount of polymeric product incorporated in the suncreening compositions herein disclosed will depend upon the exact amount of pendant groups in the polymeric backbone and the degree of protection which is desired in a particular preparation. The formulator of any particular preparation may calculate the percent of reactive suncreening groups which is ultimately in any preparation by knowing the percentage of pendant groups in the polyethylenimine polymer reaction product. The amount of pendant groups which affords ample protection is from about 0.1 to 10 percent of the total formulation. For example, protection can be attained by forming a suncreening composition containing 1.0 percent dimethylaminobenzoyl radicals.

A vehicle material is combined with the polymeric reaction products disclosed hereinabove to form suncreening compositions which can be readily dispensed onto the skin of the user. These materials may be a water-alcohol mixture, water and oil cream or an oil base, as customarily known to those skilled in the art. The water-alcohol base may contain up to 75 percent of an alcohol material having lower alkyl groups such as methanol, ethanol, propanol and the like. Alternately, or in combination, the water-alcohol vehicle material may contain dihydroxy alcohols such as ethylene glycol, propylene glycol and the like. The oil base or the oil and water cream materials may contain oils which are commonly used and are known to those skilled in the art. Examples of such oils are mineral, vegetable and animal oils. Emulsions of the suncreening polymeric reaction product may be made with any of these base materials to form a homogenous mixture which can be subsequently applied to the skin.

The compositions herein disclosed may, in addition, contain the usual quantities of additional ingredients. These ingredients include emulsifiers, fillers, perfumes, stabilizers, and the like commonly used in such preparations.

The compositions thus formed can be easily applied to the skin of the user and will readily form a film material which contains the erythema-protecting polymeric agent. In the case of a water-alcohol based material the volatile base will evaporate and leave on the skin a continuous transparent film material. Such films will provide complete and long lasting protection against ery-

thema-producing rays and it has been found that these films are not easily removed by the action of fresh or salt water or through the perspiration of the user. The oil base materials and the water and oil base compositions will form a continuous oily film of the desired polymeric suncreening material. These films also provide complete and long lasting protection against sun induced erythema. Sunscreening compositions are generally used in hot weather and at beaches where people enjoy bathing activities. It is therefore, essential that the protective coating applied to the skin is not appreciably effected by water or perspiration. The compositions herein disclosed form a thin layer of protective coating on the skin of the user and will form a long lasting material which is not easily removed by the action of fresh or salt water or through perspiration. Therefore, the compositions disclosed herein offer a more complete and efficient protection than compositions known and commonly sold on the market.

The following examples herein disclosed are for illustrative purposes only and are not meant to be limiting upon the invention concept except as set forth in the appended claims. All parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A polymeric reaction product which is formed from the reaction of dimethylaminobenzoyl chloride with a commercially available polyethylenimine having an average molecular weight of 1,800 is prepared. The resultant product having 15 percent pendant dialkylaminobenzoyl radicals as determined by an oxygen analysis has a maximum absorption peak at 298 millimicrons and is, therefore, an ultraviolet radiation absorbing material useful in preventing erythema conditions. An oil base sunscreen lotion is prepared using the above polymeric reaction product as follows:

poly(p-dimethylaminobenzoyl)ethylenimine	10 parts
mineral oil (U.S.P.)	45 parts
peanut oil	45 parts

The oily lotion is applied to the skin of a user. The film formed offered complete protection to sunburning even after several hours of bathing and being in the sun.

EXAMPLE II

A composition was prepared of the dimethylaminobenzoyl chloride and polyethylenimine reaction product as described in Example I which is incorporated into an aqueous alcoholic solution. A typical example of such a composition is as follows:

poly(p-dimethylaminobenzoyl)ethylenimine	20 parts
ethyl alcohol	30 parts
water	50 parts

Such a composition is applied to the skin and when the volatile vehicles evaporate sunscreening polymeric material forms a continuous film on the skin of the user and is found to be resistant to water and perspiration and, therefore, forms an effective longlasting protection to erythema-causing rays.

EXAMPLE III

A polymeric reaction product was prepared by react-

ing diethylaminobenzoyl chloride with polyethylenimine of 1,800 average molecular weight. The resultant product contained 20 percent by weight, based on the total weight of the polymeric material, of the diethylaminobenzoyl radical as determined by an oxygen analysis of the product. The product is incorporated into a cosmetic lotion to form an emulsion and is applied to the skin to produce a continuous film of the polymeric product upon evaporation of the more volatile vehicles. This film is durable to water and perspiration and was found to give longlasting protection to erythema causing rays.

it will be understood that it is intended to cover all changes and modifications of the examples of the invention herein chosen for the purpose of illustration which do not constitute departures from the spirit and scope of the invention.

What is claimed is:

1. A method of protecting the human skin from erythema inducing ultraviolet radiation which comprises applying to the skin a composition containing from 1 percent to about 75 percent based on the total weight of the composition of a polymeric reaction product of at least one p-di-C₁-C₄-alkylaminobenzoyl halide with polyethylenimine having an average molecular weight ranging from about 500 to 100,000 in a topical skin cosmetic carrier material selected from the group consisting of water-lower alcohol mixture, and an animal, vegetable and mineral oil base.

2. A method according to claim 1 wherein the p-dialkylaminobenzoyl halide is p-dimethylaminobenzoyl chloride.

3. A method according to claim 1 wherein the carrier material is a lotion.

4. A method according to claim 1 wherein the polymeric reaction product contains from 5 to 80 weight percent based on the total weight of the polymeric material of the residue group of p-dialkylaminobenzoyl halide.

5. A method according to claim 1 wherein the carrier material is a water-lower alkyl alcohol mixture having up to 75 percent by weight alcohol.

6. A substantive polymeric sunscreening composition comprising a polymeric reaction product of a polyethylenimine and a di-C₁-C₄-alkylaminobenzoyl halide having an average molecular weight of from about 500 to 100,000, wherein said product contains the dialkylaminobenzoyl groups pendant to the polymeric backbone and a topical skin cosmetic carrier material selected from the group consisting of water-lower alcohol mixture, and an animal, vegetable or mineral oil base.

7. A composition of claim 6 wherein the pendant dialkylaminobenzoyl groups are in a concentration ranging from about 0.1 percent to about 10.0 percent based on the total weight of the composition.

8. A composition of claim 6 wherein the dialkylaminobenzoyl halide is dimethylaminobenzoyl chloride.

9. A composition according to claim 6 wherein the cosmetic carrier is a water-lower alkyl alcohol mixture having up to 75 percent by weight alcohol.

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